

Thermal expansion of binary ionic clathrate hydrates

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Ionic clathrate hydrates are a type of inclusion compounds stabilized by ionic interaction between guest ions and charged host lattice. In this study, we verified the existence of strong ionic interaction through identifying thermal expansion of ionic clathrate hydrates by high-resolution powder X-ray diffraction. In the binary ($\text{Me}_4\text{NOH} + \text{X}$) ionic clathrate hydrate system ($\text{X} = \text{O}_2, \text{N}_2, \text{H}_2$) known to cubic $Fd\bar{3}m$ structure, obtained cell parameters at 80 K are $a = 17.1574(11), 17.1847(14),$ and $17.1239(11)$ Å and at 150 K are $a = 17.1589(26), 17.1907(30),$ and $17.1328(15)$ Å, respectively, and thus, the calculated cell parameter ratios, $a(150\text{K}) / a(80\text{K})$, are 1.000087, 1.000349, and 1.000520 respectively. Comparing to the results from nonionic hydrate, (THF + X) clathrate hydrate system having the values of 1.002 ~ 1.003, the thermal expansivity of ionic system is much smaller in spite of same host structure. This small expansion of ionic clathrate hydrates clearly due to ionic interaction might be one of important physical properties to understand ionic clathrate hydrates.